IV.E.5 Electrochemical Reversible Formation of Alane

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Project Start Date: October 1, 2011
Project End Date: Project continuation and direction
determined annually by DOE

Overall Objectives

- Develop methods of alane production and regeneration that lower the cost of alane production to less than $10/kg

- Demonstrate and characterize alane production system that lowers the cost of alane production with the lowest possible capital and operating costs

- Identify and quantify fundamental properties of alane production chemistry and physics that will lead to improved design and modeling of systems for alane production and use

Fiscal Year (FY) 2013 Objectives

- Demonstrate regeneration of the electrolyte for the electrochemical production of alane from spent alane, hydrogen, and electrochemical cell byproducts

- Improve electrochemical cell design to allow collection of individual electrode products that will enable electrolyte regeneration

- Identify methods to increase the efficiency of electrochemical alane production

Technical Barriers

This project addresses the following technical barriers from the Technical Plan - Storage section of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan:

(A) System Weight and Volume

(B) System Cost

(C) Efficiency

(Q) Regeneration Processes

Technical Targets

In this project, studies are being conducted to lower cost and improve efficiency of the electrochemical method to form AlH_3. This material has the potential to meet long-term and near-term targets for automotive and portable power applications [1,2]. The research performed as part of this contract is equally applicable to both areas.

- By 2015, develop and verify a single-use hydrogen storage system for portable power applications achieving 0.7 kWh/kg system (2.0 wt% hydrogen) and 1.0 kWh/L system (0.030 kg hydrogen/L) at a cost of $0.09/Whnet ($3/g H2 stored).

- By 2017, develop and verify onboard automotive hydrogen storage systems achieving 1.8 kWh/kg system (5.5 wt% hydrogen) and 1.3 kWh/L system (0.040 kg hydrogen/L) at a cost of $12/kWh ($400/kg H2 stored).

FY 2013 Accomplishments

- Demonstrated regeneration of $LiAlH_4$ electrolyte for electrochemical charging

- Identified a commercially available, low-cost catalyst that can be used in reasonable quantities to accomplish electrolyte recharging

- Demonstrated electrochemically active compounds and used electrochemical impedance spectroscopy to show that kinetic improvements were due to more than increased ionic conductivity

- Demonstrated a divided cell for alane electrochemistry that was able to isolate alane and Li products from the electrolysis of $LiAlH_4$

- Signed a Cooperative Research and Development Agreement with Ardica Technologies, Inc., to develop commercial alane production methods

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INTRODUCTION

The DOE is supporting research to demonstrate viable materials for onboard hydrogen storage. Aluminum hydride (alane - AlH_3), having a gravimetric capacity of 10 wt% and volumetric capacity of 149 g H_2/L and a desorption temperature of ~60°C to 175°C (depending on particle size and the addition of catalysts) has the potential to meet the 2015 and 2017 DOE targets for portable power and automotive applications. The main drawback for using alane as a hydrogen storage material is unfavorable thermodynamics towards hydrogenation. Zidan et al. [3] were the first to show a reversible cycle utilizing electrochemistry and direct hydrogenation, where gram quantities of alane were produced, isolated, and characterized. This regeneration method is based on a complete cycle that uses electrolysis and catalytic hydrogenation of spent Al(s). This cycle avoids the impractical high pressure needed to form AlH_3 and the chemical reaction route of AlH_3 that leads to the formation of alkali halide salts, such as LiCl or NaCl, which become a thermodynamic sink because of their stability.

During FY 2013, research has continued to demonstrate critical steps to the overall cycle and to improve the electrolysis cells for alane generation. Efforts to demonstrate the other parts of the alane fueling cycle include the demonstration of a method to regenerate $LiAlH_4$ from the products of the electrolysis reaction and identification of catalysts for the regeneration. Improvements in the electrochemical cell design were made for product isolation and to limit transport between the sides of the cell to a single ion. Collaborative research with Ardica has also started under a Cooperative Research and Development Agreement on methods to reduce the cost of alane production for use in commercial devices.

APPROACH

The electrochemical generation of alane has been shown by Zidan et al. [3,4] to be capable of generating high purity material using methods that can be developed into a fueling cycle for hydrogen vehicles, portable power systems, or other applications. This research has demonstrated the system electrochemistry and improvements have been made to improve the efficiency of the electrochemical alane production reactions. The regeneration of the electrolyte from spent materials and improvements in the separations process are equally as important in developing overall alane production and reprocessing schemes. SRNL has developed and demonstrated a method to regenerate the electrolyte for the electrochemical cell with materials present in electrochemical cell cathode, dehydrogenated alane, and hydrogen gas. Improvements to the electrochemical cell design have also been realized to allow improved separation of the cell products to enable electrolyte generation and separation of alane.

RESULTS

Figure 1 shows the reactor for regenerating the electrolyte for the electrochemical cell. The regeneration of the electrolyte for electrochemical alane production was performed in a Parr^{TM} reactor that can operate at elevated temperatures and pressures. The reactants for the regeneration method are lithium hydride, activated aluminum, hydrogen gas and Ti-based catalyst. These reactants simulate using the cathode product from electrochemical alane synthesis, dehydrogenated alane from a hydrogen storage application, and hydrogen for refueling. The reactants are combined with an inexpensive heterogeneous catalyst and tetrahydrofuran (THF) in the reactor. The reactor is heated to 75°C with stirring to carry out the reaction. The solids are filtered and the electrolyte is used to for the electrochemical regeneration of alane.

The $LiAlH_4$ yield for the electrolyte regeneration was above 75% with only minor adjustments to the catalyst loading of the reactor and no optimization of the reaction conditions. The reaction product contained mostly alane with other minor by-products including Al and Li_3AlH_6. Figure 2 shows an X-ray diffraction of the reaction product isolated from the solvent showing strong signals from $LiAlH_4$ with minor peaks from by-products. Previous experience with similar systems has shown that the reaction product distribution can be shifted through changes in temperature, pressure, and catalyst loading. Future work on the regeneration of the electrolyte will include increasing the yield of $LiAlH_4$ and selectivity over byproducts.

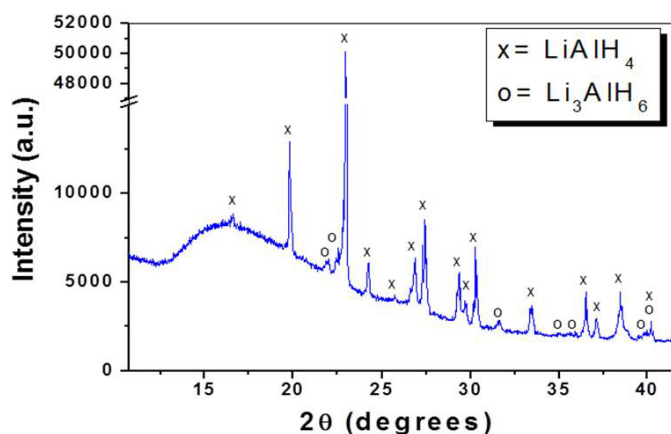**FIGURE 1.** Reactor setup for electrolyte regeneration experiments.

FIGURE 2. X-ray diffraction of the regenerated $LiAlH_4$ from Al, LiH, and H_2 in THF. The product was isolated by vacuum distillation of the solvent. The minor Li_3AlH_6 phase observed is likely due to the solvent removal process.

New electrochemical cell designs were fabricated to allow easier precipitation and collection of pure alane along with isolating the cathode product for regeneration reactions. Figure 3 shows one of the new divided cell designs. The anolyte was concentrated $LiAlH_4$ in THF and the catholyte was concentrated LiCl in THF. A Nafion® 117 membrane that had been ion-exchanged to the lithium form and dehydrated was used as the divider for the cell. Modifications to the electrode design were also made to minimize the distance of the electrodes from the membrane so that ohmic losses in the cell are reduced. There were no indications of leaking between the compartments of the cell even after five days of continuous operation.

Testing was also conducted to see how the addition of co-solvents could decrease ohmic losses in the electrochemical cell. Figure 4 shows a characterization of the ionic conductivity of 1.0 M $LiAlH_4$ as diglyme is added to the solution in small aliquots. Addition of less than 2.5 vol% diglyme caused an increase of nearly 300% in the conductivity of the electrolyte. A possible explanation for this phenomenon is the increased ionic mobility of the ions as they are complexed by the diglyme in the solution. Diglyme contains three oxygen atoms which allow it to chelate and bind to the Li^+ in solution leading to the enhanced conductivity. Addition of diglyme above 2.5% did not yield increased conductivity and a significant decrease in the solution conductivity was seen when the solution separated into two phases above 3.5 vol% diglyme.

CONCLUSIONS AND FUTURE DIRECTIONS

- Demonstrated the regeneration of the electrolyte in a Parr™ reactor with temperature and pressure

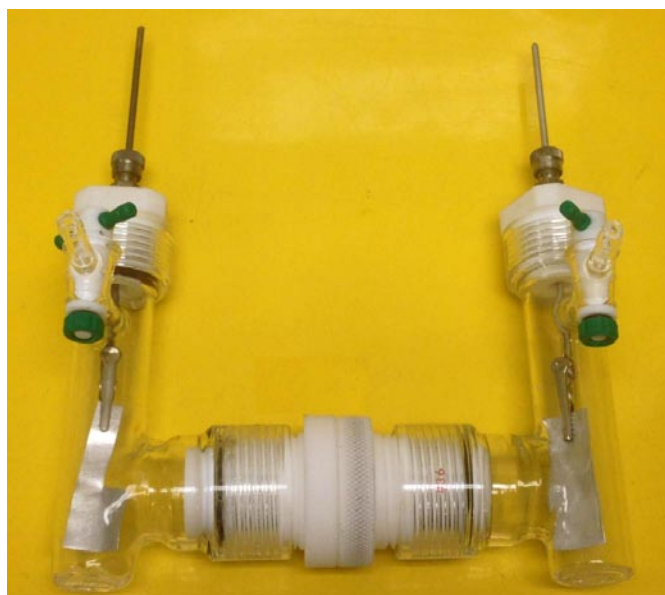- Produced $LiAlH_4$ during regeneration with 75% yield

FIGURE 3. Divided electrochemical cell design for alane production. The cell yielded pure alane and lithium metal in two separate electrodes with different electrolyte solutions.
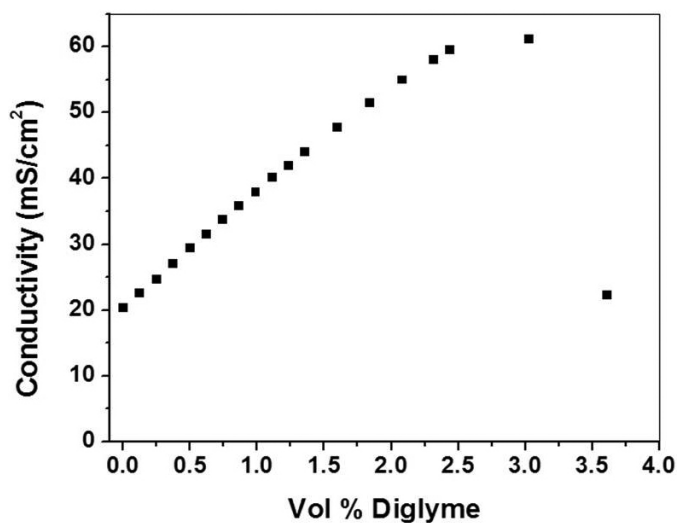

FIGURE 4. Plot of conductivity of the solution versus volume percent of added diglyme. The addition of small amounts of diglyme shows a significant improvement in the cell conductivity.

- Identified an inexpensive catalyst for the electrolyte regeneration

- Designed and tested divided electrochemical cells for alane production

- Demonstrated the effectiveness of co-solvents to significantly increase the conductivity of the electrolyte solution for alane production

SPECIAL RECOGNITIONS & AWARDS/ PATENTS ISSUED

1. Ragaiy Zidan, Douglas A. Knight, Long V. Dinh; Novel Methods for Synthesizing Alane without the Formation of Adducts and Free of Halides US20120141363 Feb 2013.

2. Ragaiy Zidan; Electrochemical Process and Production of Novel Complex Hydrides US8,470,156B2 Jun 2013.

FY 2013 PUBLICATIONS/PRESENTATIONS

1. Long V. Dinh, Douglas A. Knight, Mark Paskevicius, Craig E. Buckley and Ragaiy Zidan, "Novel methods for synthesizing halide-free alane without the formation of adducts," Applied Physics A, 2012 Vol. 107, No. 1, 173-181. [PB]

2. Joseph A. Teprovich Jr., Theodore Motyka, Ragaiy Zidan, "Hydrogen system using novel additives to catalyze hydrogen release from the hydrolysis of alane and activated aluminum," Int. J. of Hydrogen Energy 2012 Vol. 3, Issue 2, 1594-1603. [PB]

3. Ragaiy Zidan, "Development and characterization of novel hydrogen storage materials", Oct 27, 2012, International Energy Agency (IEA) HIA Task 22 Meeting Kyoto Japan. [PR]

4. "Novel Materials and New Methods for Hydrogen Storage," International Symposium on Metal-Hydrogen Systems 2012, Oct 21, Kyoto, Japan Invited Speaker. [PR]

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1. Teprovich, J.A., T. Motyka, and R. Zidan, International Journal of Hydrogen Energy, 2012. **37**(2): p. 1594-1603.

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4. Martinez-Rodriguez, M.J., et al., Appl. Phys. A-Mater. Sci. Process., 2012. **106**(3): p. 545-550.